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Young, Old, and Weathered Carbon—Part 1: Using Radiocarbon and Stable Isotopes to Identify Carbon Sources in an Alkaline, Humic Lake

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YOUNG, OLD, AND WEATHERED CARBON—PART 1: USING RADIOCARBON AND STABLE ISOTOPES TO IDENTIFY CARBON SOURCES IN AN ALKALINE, HUMIC LAKE

Evelyn M Keaveney^{1,2} • Paula J Reimer¹ • Robert H Foy^{3,4}

ABSTRACT. This article presents a case study of Lower Lough Erne, a humic, alkaline lake in northwest Ireland, and uses the radiocarbon method to determine the source and age of carbon to establish whether terrestrial carbon is utilized by heterotrophic organisms or buried in sediment. Stepped combustion was used to estimate the degree of the burial of terrestrial carbon in surface sediment. $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$, and $\delta^{15}\text{N}$ values were measured for phytoplankton, dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and particulate organic carbon (POC). $\Delta^{14}\text{C}$ values were used to indicate the presence of different sources of carbon, including bedrock-derived inorganic carbon, “modern,” “recent,” “subsurface,” and “subfossil” terrestrial carbon in the lake. The use of ^{14}C in conjunction with novel methods (e.g. stepped combustion) allows the determination of the pathway of terrestrial carbon in the system, which has implications for regional and global carbon cycling.

INTRODUCTION

The structure and function of aquatic ecosystems are strongly influenced by carbon imported from terrestrial catchments. With nutrient inputs, the relative composition and character of carbon entering lakes is a significant driver of energy mobilization and utilization by lake heterotrophs. An estimated 2.9 Pg of carbon is exported annually from terrestrial catchments to freshwater (Tranvik et al. 2009; Butman and Raymond 2011). Transfer of terrestrial carbon (e.g. plant matter, soil, peat) to higher trophic levels can be considerable in lakes with even moderately high organic loading. Increased precipitation, temperature, and consequently greater mobility of DOC lead to higher export of catchment terrestrial carbon (Vuorenmaa et al. 2006).

Elevated autochthonous photosynthetic production can lead to higher burial rates in lake sediment (Heathcote and Downing 2012). Significant loading of terrestrial carbon (TC) metabolized in the food web leads to increased pCO_2 values and consequently elevated CO_2 flux to the atmosphere (Gupta et al. 2008), while a lengthened photoperiod can increase photomineralization of DOC and elevate bacterial production (Kritzberg et al. 2006; Koehler et al. 2014). Diagenesis of carbon can lead to decreased nutrient quality, determining the likelihood of metabolization in the food web or alternatively burial in sediment.

Catchment changes (soil erosion, peat cutting, dredging, etc.) and/or extreme flood events may lead to the export of terrestrial carbon, which may supplement or supplant freshwater primary production (autochthonous). Terrestrial carbon can be derived from material of different ages. Modern terrestrial carbon is derived from photosynthetic material, contemporary with the modern atmosphere. Recent carbon can be derived from surface soil composed of recently deposited plant material that has undergone minimal decay. Subsurface or subfossil carbon previously sequestered in soil/peat stocks can be decades to centuries old (Trumbore 2000; Douglas et al. 2014).

The source of carbon in a lake also determines its biochemical composition and nutrient quality and likelihood of metabolization in the food web. Autochthonous carbon and labile terrestrial carbon released from soil minerals are relatively high-nutrient food sources and are likely to enter the food web (Caraco et al. 2010; Ishikawa et al. 2013, 2014). Older detrital TC is lower quality and so is less likely to be a nutrient resource for lake biota, precluding its selection by heterotrophic organisms (Butman et al. 2007, 2012; Ågren et al. 2008; Roiha et al. 2012).

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In light of the global increase of terrestrial loading to freshwater (Lapierre et al. 2013), the goal of this study was to determine the source and pathway of TC in Lower Lough Erne (Northern Ireland) with complex carbon dynamics, in order to address the following questions:

- What comprises the carbon pools available to autotrophic and heterotrophic organisms (modern, recent, bomb, or subfossil terrestrial organic, geological inorganic, or atmospheric carbon) in Lower Lough Erne?
- Is terrestrial carbon utilized by heterotrophic organisms [becoming a potential source of greenhouse gases (GHGs)] or is it buried in the lake sediment?

BACKGROUND

As the pathways of carbon in a freshwater lake are intrinsically linked with biotic processes, the carbon sources utilized by autotrophs and heterotrophs need to be determined.

Autotrophic Production

It has been demonstrated that $\delta^{13}\text{C}$ values of aquatic photosynthetic plants and plankton utilizing inorganic carbon in lakes are variable due to differences in carbon availability and kinetic fractionation (Farquhar et al. 1989; McConnaughey et al. 1997). Inorganic carbon is derived from the atmosphere, whereas microbial decay of terrestrial vegetation and geological weathering each represent a stable isotope and radiocarbon end member (Broecker and Walton 1959; France 1995; Carpenter et al. 2005; Cole et al. 2006; Nara et al. 2010; Zigah et al. 2011).

Stable carbon isotope analyses utilize models of photosynthetic fractionation to identify an isotopic baseline signal for phytoplankton (Karlsson et al. 2003; Pace et al. 2004). There is debate on the accuracy of these methods as it is difficult to determine whether phytoplankton utilize dissolved CO_2 or bicarbonate (Smyntek et al. 2012). There are also difficulties with sample size and isolation of phytoplankton, as well as considerable variation in phytoplankton $\delta^{13}\text{C}$ values depending on carbon source (Carpenter et al. 2005; Bade et al. 2006; Smyntek et al. 2012). Isotopic food web studies require separation between different sources, but baseline autotrophic $\delta^{13}\text{C}$ signals are sufficiently variable to overlap with other end members (Ishikawa et al. 2013).

Heterotrophic Metabolization of Organic Carbon

Debate remains as to processes by which dissolved and particulate organic carbon (DOC and POC, respectively) are utilized by lake heterotrophs in addition to the fraction of each consumed (Bartels et al. 2012; de Kluijver et al. 2012; Wilkinson et al. 2013). The biochemical composition and resulting nutrient value (biochemical quality) of DOC or POC governs selection as a food source, yet stable isotope end members are often insufficiently distinct to distinguish them as carbon sources to aquatic consumers.

Many studies suggest the biochemical quality of the organic input is an important factor governing its fate in lakes, and this may explain why in some lakes DOC is the predominant terrestrial carbon source utilized by zooplankton (Taipale et al. 2007, 2008; McCallister and del Giorgio 2008; Zigah et al. 2011; de Kluijver et al. 2012). Seasonality is an inherent characteristic of temperate lakes with alternation between high summer to low winter autochthonous production according to changes in light and temperature, which affect the magnitude and temporal delivery of nutrients (Grey et al. 2001; Kritzberg et al. 2006; Neff et al. 2006; Rautio et al. 2011). Carbon fixed by phytoplankton and algae is bio-energetically rich compared to the bulk of the terrestrial organic input to lakes due to prior diagenesis. Accordingly, lake heterotrophs tend to optimize their feeding to exploit such

dietary sources. Thus, the carbon source maintaining but also producing biomass can shift considerably with the seasonal availability of resources (Maguire and Grey 2006; Rautio and Vincent 2007; Taipale et al. 2008; Rautio et al. 2011).

Using ^{14}C to Determine Carbon Source

Natural-abundance ^{14}C analysis can be used to clarify lake carbon dynamics that cannot be explained using stable isotope analysis alone. $\Delta^{14}\text{C}$ (see Methods for derivation) of freshwater carbon is governed by its source. Normalization of ^{14}C values (see Methods) negates the issue of kinetic fractionation, allowing for the isolation of a baseline isotopic signature and accurate separation of individual carbon sources. Low natural abundance of the ^{14}C atom allows for a more sensitive approach to source partitioning than stable carbon isotope analysis. $\Delta^{14}\text{C}$ values distinguish between carbon sources since relatively minor isotopic changes are amplified due to the low ^{14}C abundance in a sample.

For the purposes of this study, the following five terms were utilized to describe the source and age of carbon in the lake:

1. *Modern* terrestrial carbon is derived from photosynthetic material contemporary to the modern atmosphere.
2. *Recent* terrestrial dissolved and particulate organic carbon can be exported from surface soil and may be derived from recently deposited plant material that has undergone minor decomposition.
3. *Subsurface* terrestrial soil stocks may incorporate ^{14}C that has a distinct bomb signal, enriched relative to the modern atmosphere due to nuclear testing in the 1950s and 1960s and resulting in positive $\Delta^{14}\text{C}$ values (Reimer et al. 2004). However, due to soil carbon cycling and turnover, atmospheric carbon with enriched $\Delta^{14}\text{C}$ can take decades to reach subsurface soil stocks (Trumbore et al. 1989; Polsemaere et al. 2013). Carbon from subsurface soil or peat may therefore have a positive $\Delta^{14}\text{C}$ value, enriched relative to the modern atmosphere.
4. *Subfossil* carbon originates from terrestrial carbon stored in soil/peat stocks that can be considerably ^{14}C depleted depending on the age of stored carbon (MacDonald et al. 1991; Raymond et al. 2004; Caraco et al. 2010).
5. *Autochthonous* carbon is generated from primary production, which utilizes dissolved inorganic carbon that is partially derived from the weathering (via atmospheric CO_2 or soil carbon) of carbonaceous bedrock with no ^{14}C content (^{14}C -dead) leading to ^{14}C -depleted DIC values (Deevey et al. 1954; Broecker and Orr 1958; Broecker and Walton 1959). Measurements from fish and water samples from a number of lakes in Ireland and Britain in 2007 indicated that a hardwater offset may be estimated from lake carbonate alkalinity ($R^2 = 0.66$, $p < 0.01$, Keaveney and Reimer 2012) with the caveat that large variations can be present due to fluctuating terrestrial inputs, particularly in oligotrophic (nutrient-poor) lakes. ^{14}C and stable isotope measurements of inorganic and organic carbon pools (DIC, DOC, and POC), photoautotrophs, and heterotrophs can therefore provide a means to assess the importance of terrestrial carbon cycling in aquatic primary production and to resolve the following hypotheses:
 - Modern terrestrial and autochthonous carbon is preferentially metabolized by lake heterotrophs, leading to CO_2 saturation and probable flux to atmosphere.
 - Subfossil terrestrial carbon is not consumed by lake heterotrophs and is buried in sediment.

METHODS

Study Site

We selected Lough Erne, Northern Ireland (Figure 1), primarily because in a previous study (Keaveney and Reimer 2012), it did not follow the trend of increasing ^{14}C offsets from the atmosphere with increased carbonate alkalinity. A great deal of research on past environmental records has also been carried out on the lake (Gibson et al. 1980, 2003, 2005; Battarbee 1986, 1984; Foy et al. 1993; Maguire and Gibson 2005) and the lake is regularly monitored by the Agricultural Food and Biosciences Institute (AFBI) of Northern Ireland, providing water chemistry data as part of the UK Environmental Change Network (ECN).

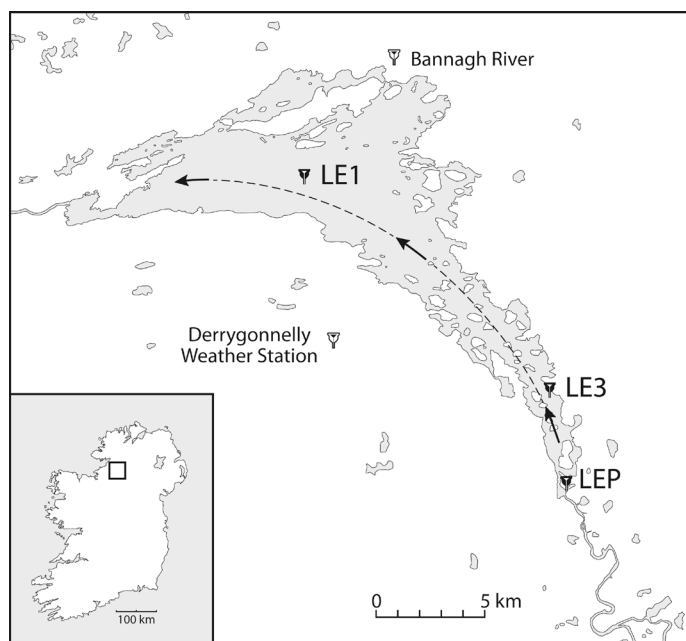


Figure 1 Lower Lough Erne, Fermanagh, Northern Ireland. Lake and river sites that were sampled are marked on the map. LE1, LE3, and LEP are represented by black markers (Table 2). Arrows show the direction of water flow.

Previous research has been conducted in the lake using stable isotope analysis (Maguire and Grey 2006) and ^{14}C analysis (Keaveney and Reimer 2012). The results of stable isotope analysis from Maguire and Grey (2006) showed that calanoid zooplankton $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values changed after zebra mussel (*Dreissena polymorpha*) invasion in the late 1990s, displaying increased reliance on terrestrial carbon with seasonal variation. The stable isotope research could not give any information on the age or source of terrestrial carbon utilized by biota in the lake. However, previous ^{14}C measurements suggested that the age of carbon subsidizing the food web was variable. Keaveney and Reimer (2012) demonstrated that although ^{14}C depletion was evident, related to the alkalinity of the lake, values were more enriched than expected due to terrestrial inputs to the lake. Further research was therefore needed to investigate the source and age of carbon in the lake to determine what was removed from downstream transport through burial. This study was carried out to build upon research previously undertaken in Lower Lough Erne, and to clarify the carbon dynamics in this complex lake.

Lough Erne is comprised of an upper and lower Lough and is the second biggest lake system in Northern Ireland. Lower Lough Erne (Figure 1, Tables 1 and 2) is downstream from the Upper Lough; 80% of water flow is from the River Erne via the Upper Lough. It has a surface area of 109 km², a catchment area of 4200 km², a maximum depth of 55 m, and a water residence time of 0.45 yr. The lake is alkaline and eutrophic, with concentrations of total phosphorus (TP) > 50 µg L⁻¹ since 1975 (Gibson et al. 1980, 2003, 2005; Battarbee 1986; Foy et al. 1993). The lake catchment (4200 km²) drains a predominately lowland glaciated drumlin landscape with gleyed soils, which are predominantly used for grass production and beef production. The geology is dominated by Carboniferous limestone, and Carboniferous, Silurian, and Ordovician sandstones and shales.

Table 1 Attributes of Lower Lough Erne study site (Zhou et al. 2000; Gibson et al. 2005).

Lake surface area	109 km ²
Max depth	55 m
Thermocline	30 m
Residence time	0.45 yr
Catchment size	4200 km ²
Summer stratification	Weak
Thermocline duration	May/June to July/August
(Upper Lough Erne residence time)*	28 days

*Environmental Change Network and R Foy (personal communication).

Table 2 Coordinates of Upper and Lower Lough Erne, River Bannagh, and Derrygonnelly weather station sampling sites (Figure 1).

Site ID	Coordinates
River Bannagh	54°32'02"N, 7°46'55"W
LE1	54°29'07"N, 7°50'37"W
LE3	54°23'51"N, 7°40'12"W
LEP	54°21'30"N, 7°39'40"W
Derrygonnelly Weather station	54°25'04"N, 7°49'20"W
Lower Lough Erne 2014	54°27'10"N, 7°44'28"W
Upper Lough Erne 2014	54°13'01"N, 7°31'41"W

During 2000 and 2001, a population explosion of the zebra mussel lowered lake and inflowing chlorophyll *a* by ~80% and low chlorophyll *a* concentrations that persisted in measurements taken during the study period in 2011 (Table 3; Keaveney et al. 2015 [this issue]). Although these algal reductions resulted in marked increases in water transparency, the presence of peat stain in the Lough water resulted in Secchi depths <3 m. Summary mean concentrations for total phosphorus, soluble reactive phosphorous, and total oxidized nitrogen for 2011 are listed in Table 3.

Weak summer stratification does periodically occur although the lake did not stratify during the study. Approximately 80% of the annual inflow is via the River Erne that enters the lake at Portora. The cumulative flow from 26 February to 26 August was equivalent to 0.54 lake volumes compared to a flow equivalent to 2.5 lake volumes for the whole of 2011; inflow to the lake is low relative to the volume of the lake. The lake lies on an approximate southeast to northwest axis; downstream from Portora the lake gradually widens into a flooded drumlin landscape with many islands and shallow depths (<10 m).

Table 3 Attributes of Lower Lough Erne sampling sites provided by the Agricultural Food and Biosciences Institute (AFBI); $p\text{CO}_2$ measurements courtesy of Christopher Barry.

Attribute	Units	Direction of flow →		
		LEP	LE3	LE1
Chlorophyll <i>a</i>	mg L ⁻¹	3.1	7.6	2.1
Total phosphorous	mg L ⁻¹	67	77	54
Soluble reactive phosphorus	mg L ⁻¹	36	35	36
Total oxidized nitrogen	mg L ⁻¹	296	328	646
pH		7.8	7.96	8.03
Conductivity	mS cm ⁻¹	239	235	230
Alkalinity	meq L ⁻¹	1.72	1.68	1.58
$p\text{CO}_2$	matm/ppm	1517	1147	696
DOC	mg L ⁻¹	19.9	19.8	16.9
Secchi disc	m	1.3	1.3	2.3

Samples were collected from a boat at three sites in the Lower Lough, abbreviated as LEP, LE3, and LE1 (Figure 1), during 2011. The LEP sampling site is located where the River Erne enters at Portora, LE3 is 3 km downstream from LEP, and LE1 is 15 km further downstream. LE1 corresponds to the open-water site known as the Broad Lough and is located at the deepest part of the lake (55 m). The hydro-geomorphology of the lake suggests that there is minimal water movement from the Broad Lough upstream towards the inflow at Portora, evidenced by the distinct phytoplankton floras of the Broad Lough in comparison to upstream shallow areas (Gibson et al. 1980; Batterbee 1984). DIC from one Upper Lough site was measured in 2014 (see Table 2 for location data).

Field Sampling for Isotopic Analyses

Field sampling for isotopic analyses was conducted in the Lower Lough in February, March, May, July, August, and October of 2011. Additional DIC samples were obtained from the Upper Lough and Lower Lough in July 2014. Water samples for stable isotope and ^{14}C DIC, DOC, and POC analyses were taken in acid-washed (10% HCl) Nalgene® polyethylene bottles prerinsed with lake water. Samples were collected under water and care was taken to ensure exposure to air was minimal. DIC was obtained by adding BaCl_2 followed by NaOH in the field to precipitate BaCO_3 (Landmeyer and Stone 1995). Plankton and invertebrate samples were collected at all sampling sites by vertical net tows of the water column (63- and 250- μm mesh sizes, respectively). In order to achieve sufficient matter for isotopic analysis, nets were trawled behind the boat during the winter months when plankton abundances were low.

Laboratory Pretreatment

POC was filtered onto Whatman® glass fiber filters (Grade C with nominal pore size 1.2 μm), which had been combusted overnight at 500°C. The filters were cut in two and acidified; one half was used for stable isotope analysis and one half for ^{14}C measurement. DOC was obtained by concentrating the sampled lake water using rotary evaporation; DOC was then separated for stable isotope and ^{14}C measurement. Algal and invertebrate samples were halved for stable isotope and ^{14}C measurements; invertebrate samples were homogenized prior to analysis using a Retsch MM200 Mixer Mill. BaCO_3 precipitate was filtered from lake water samples and collected on filters for DIC measurement (detailed pretreatment methods for all samples can be found in the [online supplemental information](#)).

Radiocarbon Measurement

Invertebrate, algae, POC, and DOC samples were loaded into precombusted quartz tubes with silver and copper oxide, sealed under vacuum, and combusted at 850°C overnight to generate CO₂ gas. DIC samples were acidified with 86% orthophosphoric acid and the CO₂ gas was cryogenically collected.

Stepped Combustion

Stepped combustion followed the method of McGeehin et al. (2001). Bulk sediment samples were halved, acidified with 4% HCl, and dried; 1 aliquot was combusted normally at 850°C overnight. The second aliquot was initially combusted at 400°C overnight before the CO₂ produced from the low-temperature combustion was collected. The remainder of the sample was recombusted at 850°C overnight and gas produced from the high-temperature combustion was again collected.

Graphitization and AMS Analysis

CO₂ gas collected from each sample was graphitized in the presence of an iron catalyst at 560°C for 4 hr according to the Bosch–Manning hydrogen reduction method (Manning and Reid 1977; Vogel et al. 1984) and analyzed on a 0.5MV National Electrostatics compact accelerator mass spectrometer (AMS) at the ¹⁴CHRONO Centre in Queen's University Belfast. The ¹⁴C/¹²C ratio of the sample relative to an international standard (F¹⁴C) and its associated uncertainty were calculated according to Reimer et al. (2004) and van der Plicht and Hogg (2006) and incorporated a fractionation correction (Stuiver and Polach 1977) based on δ¹³C measured by AMS.

Δ¹⁴C is defined in Stuiver and Polach (1977) as the relative difference between the absolute international standard (base year 1950) and sample ¹⁴C/¹²C ratio corrected for age and δ¹³C fractionation. The Δ¹⁴C age correction accounts for decay that took place between collection/death and the time of measurement, which is calculated using the equation

$$\Delta^{14}\text{C} = [\text{F}^{14}\text{C} * e^{\lambda(1950-x)} - 1] * 1000$$

where x is the year of growth (2011 for this study) and F¹⁴C is the ratio of the sample ¹⁴C/¹²C and standard ¹⁴C/¹²C, both corrected for isotope fractionation (Reimer et al. 2004).

The AMS δ¹³C values include any fractionation that may occur during sample preparation and AMS analysis. These values are used for fractionation correction only, so will not be further discussed here. All other stable isotope measurements were made using a Thermo Scientific Delta V Advantage EA-IRMS. Samples were corrected using a one-point calibration with the standard IA-R041 L-alanine (δ¹³C = −23.33‰; δ¹⁵N = −5.56‰). Two other standards were measured at intervals: USGS41 L-glutamic acid (δ¹³C = +37.63‰; δ¹⁵N = +47.57‰) and leucine (δ¹³C = −30.52‰; δ¹⁵N = +10.77‰) and results plotted to make a two-point calibration. The effect of applying one-point and two-point correction to samples was compared and the difference was negligible. The precision of the EA-IRMS is <0.1‰ for δ¹³C and <0.15‰ for δ¹⁵N.

Lake Water Analyses

During the study period and at approximately 14-day intervals, surface water samples were taken at each site together with a 0–10 m integrated sample at the LE1 site as set out by Foy et al. (1993). Sampling included *in situ* measurements of lake water temperature and Secchi disc depth. On return to the laboratory, samples were analyzed for chlorophyll *a*, nutrients, alkalinity, and pH using standard methods as described by Girvan and Foy (2006). Summary mean values for the period 2011 are listed in Table 3 plus means for lake water DOC, which was determined within 24 hr by

Pt-catalyzed combustion (Teledyne Techmar Apollo 9000 TOC analyzer). Between January and September 2011, nine sets of *in situ* measurements of carbon dioxide partial pressure ($p\text{CO}_2$) in surface water (0.4 m depth) were also using an EGM-4 portable infrared gas analyzer (PP Systems, UK).

RESULTS

Comprehensive tables of results can be found in the [online supplemental information](#).

Inorganic Carbon and Autotrophic Producers

Carbon sources (terrestrial and/or rock-derived) supporting the inorganic carbon pool can be examined using DIC $\Delta^{14}\text{C}$. Values are spatially and temporally variable in Lower Lough Erne. DIC $\Delta^{14}\text{C}$ should be depleted relative to the contemporary atmosphere caused by the hardwater effect due to the carbonate alkalinity of the lake (expected value $\Delta^{14}\text{C} \approx -63\text{‰}$, Keaveney and Reimer 2012). However, the spatial and temporal variation seen in Figure 2 is different from the DIC value expected from the consistent alkalinity of the lake water. There is substantial enrichment of DIC $\Delta^{14}\text{C}$ values (Figure 2) measured from LE1 in May ($\Delta^{14}\text{C} = -20.0 \pm 3.6\text{‰}$) relative to those measured in February and March ($\Delta^{14}\text{C} = -55.5 \pm 3.0\text{‰}$ and $-54.4 \pm 3.1\text{‰}$, respectively).

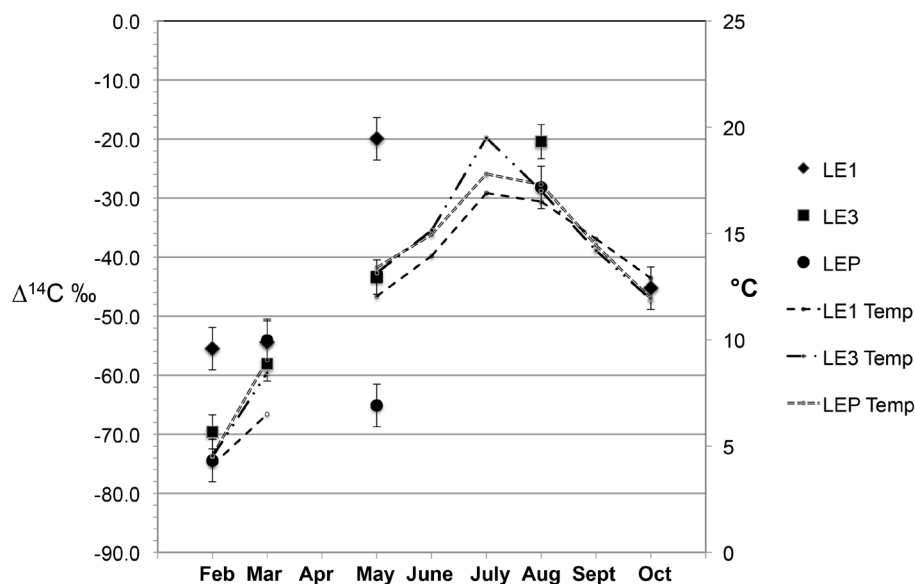


Figure 2 DIC $\Delta^{14}\text{C}$ values ([supplemental information](#)) plotted with average monthly lake water temperatures from each site. Error bars correspond to 1σ uncertainty on $\Delta^{14}\text{C}$ measurements.

There is also spatial variation in DIC $\Delta^{14}\text{C}$. LE3 and LEP values are more depleted than LE1 ($\Delta^{14}\text{C} = -65.8 \pm 6.6\text{‰}$ and $-64.6 \pm 10.2\text{‰}$, respectively). Both become enriched in August ($\Delta^{14}\text{C} = -20.5 \pm 3.5\text{‰}$ and $-28.2 \pm 3.9\text{‰}$, respectively). DIC $\Delta^{14}\text{C}$ from Upper Lough Erne (Table 2) measured in July 2014 is comparable to that of samples collected from LE3 and LEP in February 2011 ($\Delta^{14}\text{C} = -76.3 \pm 4.5\text{‰}$).

The temporal and spatial variability evident in DIC values was not present in algal $\Delta^{14}\text{C}$ values (Figure 3) collected in the year of study on the same day as DIC and other samples ($\Delta^{14}\text{C} = -50.4 \pm 22.1\text{‰}$). Samples collected in May (dominated by cyanobacteria) were ^{14}C -depleted ($\Delta^{14}\text{C} = -93.4 \pm 4.5\text{‰}$) relative to DIC ^{14}C (mean DIC from all sites in May: $\Delta^{14}\text{C} = -51.6 \pm 27.5\text{‰}$) and algae collected throughout the year. Cyanobacteria collected in August ($\Delta^{14}\text{C} = -57.9 \pm 3.9\text{‰}$) were ^{14}C -enriched relative to the single depleted May sample value. Algal samples collected in February

when algal abundance was low (mean $\Delta^{14}\text{C} = -51.5 \pm 29.6\text{‰}$) were dominated by cyanobacteria and are consistent with August measurements.

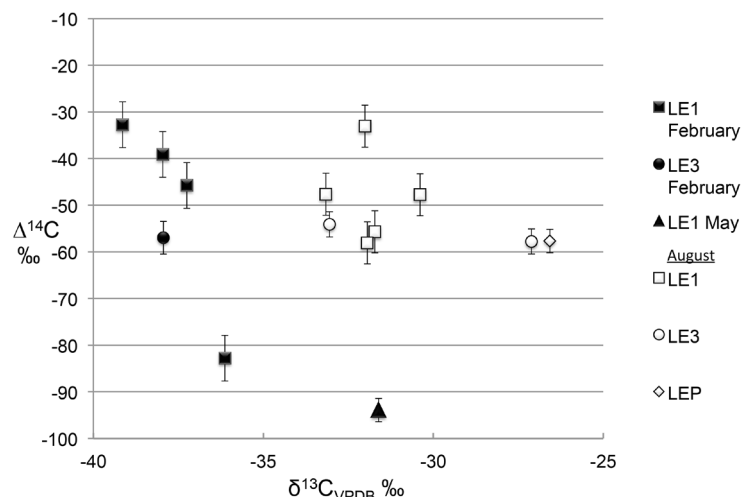


Figure 3 Algae and cyanobacteria carbon isotope values. Samples were collected in February, May, and August 2011. The samples in February and May were difficult to analyze due to low algal abundance but were dominated by cyanobacteria. Increased algal abundance allowed separation of species in August ([supplemental information](#)). Error bars correspond to 1σ uncertainty on $\Delta^{14}\text{C}$ measurements.

Terrestrial Carbon

DOC samples taken from the lake are ^{14}C -enriched relative to other carbon pools, and, although DOC $\Delta^{14}\text{C}$ is variable over the sampling period (mean $\Delta^{14}\text{C} = -16.5 \pm 8.6\text{‰}$, Figure 4), values are also equivalent to POC and DOC samples from the tributary River Bannagh ($\Delta^{14}\text{C} = -29.9 \pm 8.2\text{‰}$ and $-16.7 \pm 3.0\text{‰}$, respectively). A positive $\Delta^{14}\text{C}$ signature was measured in DOC collected from the River Bannagh in October ($+50 \pm 2.9\text{‰}$). POC samples are consistently more ^{14}C -depleted (mean $\Delta^{14}\text{C} = -122.3 \pm 32.6\text{‰}$) than other samples.

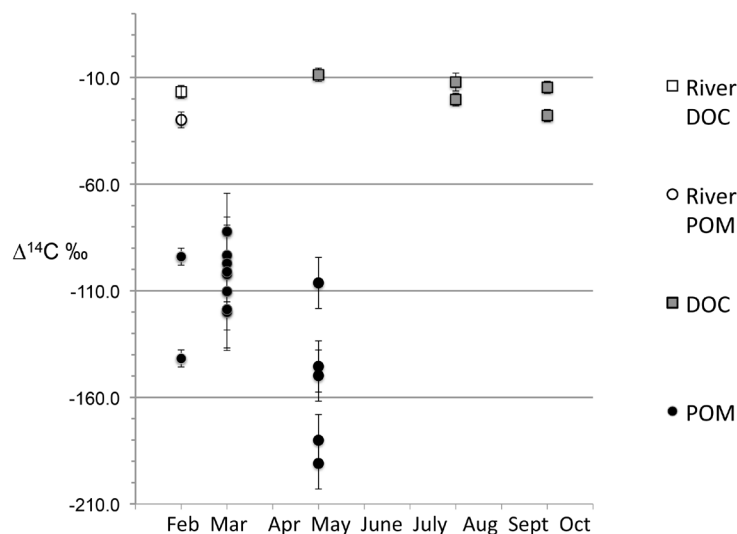


Figure 4 $\Delta^{14}\text{C}$ values of DOC and POC collected from Lower Lough Erne and River Bannagh in 2011. Error bars correspond to 1σ uncertainty on $\Delta^{14}\text{C}$ measurements.

Lake Sediment: Stepped Combustion

Stepped combustion of lake surface sediment yielded distinct $\Delta^{14}\text{C}$ values (Figure 5). Figure 6 illustrates the difference between the samples. Samples that combusted at a higher temperature were ^{14}C -depleted ($\Delta^{14}\text{C} = -167.2 \pm 3.7\text{‰}$, $-173.4 \pm 3.7\text{‰}$) relative to bulk sediment samples ($\Delta^{14}\text{C} = -134.0 \pm 3.9\text{‰}$, $-127.3 \pm 3.5\text{‰}$, Table 5). The sample combusted at 400°C was ^{14}C -enriched ($\Delta^{14}\text{C} = -68.1 \pm 3.6\text{‰}$) relative to the bulk sediment.

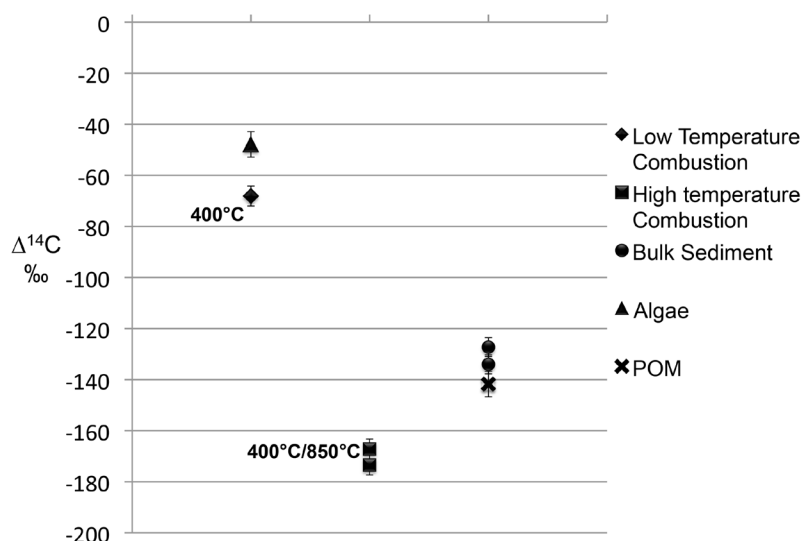


Figure 5 $\Delta^{14}\text{C}$ values of Lower Lough Erne sediment compared with algae and POC values. Error bars correspond to 1σ uncertainty on $\Delta^{14}\text{C}$ measurements.

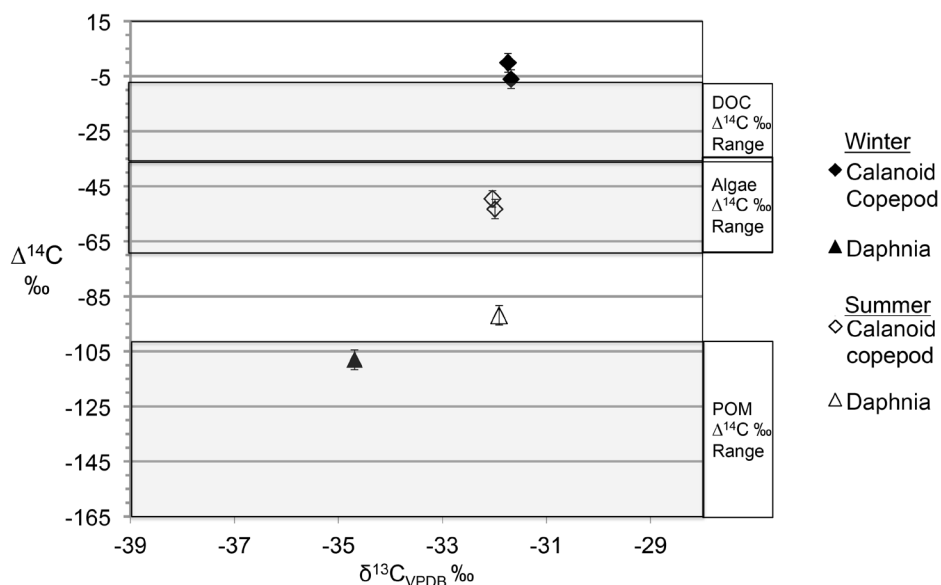


Figure 6 Invertebrate $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of selected Lower Lough Erne zooplankton. Winter samples were collected in February and March, and summer samples in August 2011. Error bars correspond to 1σ uncertainty on $\Delta^{14}\text{C}$ measurements.

Invertebrate Community

The zooplankton measured comprised calanoid zooplankton (*Eudiaptomus gracilis*) and *Daphnia* spp. Other invertebrates were also collected but sample size was relatively small. Seasonal variation and differences in carbon source were evident in selected invertebrates presented in this study.

Herbivorous calanoid zooplankton $\Delta^{14}\text{C}$ values (Figure 6) were enriched relative to the $\Delta^{14}\text{C}$ signature of their preferred food source, algae. The mean calanoid zooplankton $\Delta^{14}\text{C}$ ($-4.0 \pm 6.1\text{‰}$) collected in winter is enriched relative to that in the summer ($\Delta^{14}\text{C} = -50 \pm 4.1\text{‰}$). The summer values are equivalent to algal $\Delta^{14}\text{C}$; winter values are equivalent to lake DOC, suggesting a change in the food source. *Daphnia* $\Delta^{14}\text{C}$ values were depleted relative to anything else in the invertebrate community (mean $\Delta^{14}\text{C} = -100 \pm 11.5\text{‰}$); they were, however, in the range of subfossil POC $\Delta^{14}\text{C}$.

DISCUSSION

The $\Delta^{14}\text{C}$ values of DIC, DOC, and POC collected from Lower Lough Erne in February indicate that there is a significant difference in age of carbon among these three pools: enriched (modern, recent, subsurface) DOC, depleted (subfossil) POC, and intermediate (geological) DIC values. Invertebrate species utilized carbon from all three pools; sediment $\Delta^{14}\text{C}$ indicated that bulk samples were dominated by subfossil terrestrial carbon.

Inorganic Carbon Pool

The DIC $\Delta^{14}\text{C}$ seen in Lower Lough Erne is enriched relative to the value predicted by Keaveney and Reimer (2012) from the carbonate alkalinity of the lake ($\approx -63\text{‰}$). Temporal variation is clear as $\Delta^{14}\text{C}$ values of DIC from sites in August are considerably enriched relative to this value. It is difficult to explain the variation in DIC $\Delta^{14}\text{C}$ particularly when the hydrology of the lake is examined. Some 80% of the flow is via the River Erne from the Upper Lough and water flows from LEP \rightarrow LE3 \rightarrow LE1; ^{14}C signals should reflect those of the Upper Lough.

The Upper Lough is dominated by macrophytes. Their proliferation and utilization of inorganic carbon may lead to incursion of atmospheric CO_2 when lake $p\text{CO}_2$ drops below atmospheric levels (Bornette and Puijalon 2011). However, DIC values measured in Upper Lough Erne in 2014 are more ^{14}C -depleted ($\Delta^{14}\text{C} = -76.3 \pm 4.5\text{‰}$) than any of the Lower Lough Erne values measured in 2011.

A decrease in $p\text{CO}_2$ values was observed along the direction of flow from LEP to LE1 (Table 3), but as the lake remains supersaturated, there is no evidence to suggest that DIC $\Delta^{14}\text{C}$ enrichment/depletion is related to CO_2 transfer between the lake and the atmosphere. DIC $\Delta^{14}\text{C}$ was enriched at all sites in summer months when all sites were supersaturated, precluding the possibility that atmospheric incursion was responsible for enrichment in the Lower Lough.

There is an insignificant pattern ($R^2 = 0.32$) of enrichment of DIC $\Delta^{14}\text{C}$ values with increased lake water and atmospheric temperatures (Figure 2). While the link between temperature and DIC values in the Lough is tenuous, an atmospheric temperature increase may lead to increased subsurface soil carbon mobility (Fang et al. 2005; Winterdahl et al. 2011), which can be remineralized (by bacteria or photomineralization) and may contribute to the inorganic carbon pool (Kritzberg et al. 2006, 2014; Tranvik et al. 2013).

The turnover time of soil can vary. While labile carbon turns over rapidly, the intermediate carbon pool in soils can take decades to decompose and the more passive soil pools turnover on a centennial scale (Trumbore et al. 1989; Torn et al. 2013). Subsurface terrestrial soil exports may therefore

incorporate bomb carbon from the last few decades. DOC containing this bomb carbon may then be rapidly remineralized once released, particularly when increased sunlight and photoperiod leads to increased photomineralization of terrestrial carbon (Tranvik et al. 2013). Thermal sensitivity of the respiration of soil carbon and subsequent increased mobility is related to microbial metabolism, which also increases with temperature (Fang et al. 2005; Liu 2013).

In order to explain enrichment of DIC $\Delta^{14}\text{C}$ values from winter to summer values, highly positive bomb $\Delta^{14}\text{C}$ must be introduced to the DIC pool. Some 80% of the flow of water to the lake is from the River Erne, yet DIC measured from the river ($n = 1$) is ^{14}C -depleted (as is the Upper Lough); the source of ^{14}C enrichment in the Lower Lough therefore cannot be autochthonous. The source of enrichment of DIC $\Delta^{14}\text{C}$ can only be derived from the remaining 20% of the water input to the lake from the catchment.

The following simple mass balance model was used to estimate the $\Delta^{14}\text{C}$ value required to enrich LE1 DIC $\Delta^{14}\text{C}$ in August (the most positive DIC $\Delta^{14}\text{C}$ value in our study):

$$Z_{\text{LAKE}} = Z_{\text{ALK}}(1-X) + X(Z_{\text{SOURCE}})$$

where Z_{LAKE} is the measured DIC $\Delta^{14}\text{C}$ from sample UBA-17857 ($\Delta^{14}\text{C} = -20\text{‰}$), Z_{ALK} is the DIC $\Delta^{14}\text{C}$ value ($\Delta^{14}\text{C} = -63\text{‰}$) estimated from the water alkalinity (Keaveney and Reimer 2012), and Z_{SOURCE} is the source end member.

Three different source end members were employed to estimate which is the most likely source of enriched ^{14}C (Table 4). Atmospheric CO_2 $\Delta^{14}\text{C}$ was obtained from the literature (Levin et al. 2013). River DOC measured in October (UBA-20706, see [online supplemental information](#)) had a positive $\Delta^{14}\text{C}$ value, so was selected to represent modern photosynthetic carbon derived from autumnal leaf fall. Given that catchment inflow to the lake is low ($\sim 20\%$), the models utilizing modern atmospheric and riverine DOC end members require unreasonably large contributions to result in the DIC $\Delta^{14}\text{C}$ values measured from Lower Lough Erne. Subsurface soil was not measured, but the end member value was chosen from values observed in soil carbon turnover studies (Koarashi et al. 2012; Torn et al. 2013; Trumbore and Schrumpp 2013), which resulted in a percent contribution that matched the catchment flow of 20%.

Table 4 Components of mass balance model to determine causes of DIC $\Delta^{14}\text{C}$ enrichment.

	End member	Z_{LAKE}	Z_{SOURCE}	Z_{ALK}	
Model	Model source	UBA-17857 DIC $\Delta^{14}\text{C}$	$\Delta^{14}\text{C}$ source	$\Delta^{14}\text{C}$ lake DIC	% contribution
1	Atmospheric	-20	40	-63	42
2	River DOC	-20	50	-63	38
3	River Erne	-20	-40	-63	-87
4	Subsurface soil	-20	152	-63	20

A hypothetical $\Delta^{14}\text{C}$ value of 152‰ results in a 20% contribution, matching the observed catchment flow rate. This bomb $\Delta^{14}\text{C}$ value can only be sourced from subsurface soil stocks (Koarashi et al. 2012; Torn et al. 2013), the contribution of which may fluctuate seasonally. Previously sequestered terrestrial carbon may be exported as temperatures increase in the summer, leading to DIC enrichment measured in the lake.

Algal Production – Utilizing Terrestrial Carbon?

With a few exceptions, algal $\Delta^{14}\text{C}$ values (mean $\Delta^{14}\text{C} = -50.4 \pm 13.3\text{‰}$) are more consistent both spatially and temporally (Figure 3), yet some are enriched relative to the value ($\Delta^{14}\text{C} \approx -63\text{‰}$) predicted from Keaveney and Reimer (2012). This indicates that algae are also relying on the inorganic pool partially derived from terrestrial carbon, although algal $\Delta^{14}\text{C}$ values are less variable than DIC $\Delta^{14}\text{C}$.

Algal (dominated by cyanobacteria) $\Delta^{14}\text{C}$, collected in May, is significantly ($>2\sigma$) more depleted ($-93.9 \pm 4.5\text{‰}$) than that of DIC collected in May, or other algal samples collected in February and August. Terrestrial POC may have been introduced into the bulk algal sample during filtration from lake water when algal abundance was low, possibly explaining the depleted $\Delta^{14}\text{C}$ value.

Organic Carbon Pools

The influence of terrestrial carbon is clearly evident in the organic carbon pools (DOC and POC, Figure 4). Enriched (modern and/or recent surface) terrestrial carbon is found in the DOC pool and depleted (subfossil) in the POC pool. Organic carbon pools in Lower Lough Erne are predominantly derived from terrestrial sources, as evidenced by the $\Delta^{14}\text{C}$ values.

$\Delta^{14}\text{C}$ values are enriched in DOC samples relative to the other carbon pools and are consistent spatially and temporally over the sampling period (Figure 4). They are also equivalent to DOC and POC samples from the tributary River Bannagh. The DOC pool is therefore seen as representative of terrestrial carbon, originating from surface soil/peat, probably entering the lake via tributary rivers. The negative $\Delta^{14}\text{C}$ values indicate they are probably derived from recently deposited leaf litter/soil carbon that has undergone some decay.

$\Delta^{14}\text{C}$ values of POC samples are consistently depleted compared to other samples, indicating they are derived from subfossil detrital terrestrial carbon (Figure 4). POC also likely contains a more modern source of carbon as well as subfossil carbon (possibly explaining variation seen in $\Delta^{14}\text{C}$ values of different samples) as indicated by stepped-combustion analysis of sediment.

The low-temperature stepped-combustion fraction yielded measurements with $\Delta^{14}\text{C}$ values equivalent to those from algae, while the high-temperature fraction subfossil values were more ^{14}C -depleted than terrestrial POC. The bulk sediment sample $\Delta^{14}\text{C}$ suggests that 64% of the buried carbon, which is more depleted than anything else in the lake, was derived from a detrital subfossil terrestrial source. It is also likely that POC is comprised of subfossil and labile carbon given its depleted $\Delta^{14}\text{C}$ value, equivalent to that of bulk sediment.

Carbon Sources of the Invertebrate Community – Autochthonous or Terrestrial?

Stable isotope values of Lower Lough Erne invertebrates measured in the current study support the assertion of Maguire and Grey (2006) that terrestrial carbon is utilized by calanoid species in the lake; ^{15}N values of calanoid copepods measured in this study are enriched more than anything else in the food web. This indicates the presence of a microbial loop with bacteria metabolizing terrestrial carbon for use by other species. However, the stable isotope results do not indicate whether the terrestrial source carbon source is DOC or detrital POC.

E. gracilis is an herbivorous calanoid copepod that usually feeds on phytoplankton. In winter months, when algal abundance is low, *E. gracilis* can supplement its diet with terrestrial carbon. Rautio et al. (2011) showed that the $\delta^{13}\text{C}$ of calanoid copepods did not track the $\delta^{13}\text{C}$ values of the POC, suggesting that they did not consume carbon from the POC pool in oligotrophic subarctic Lake Saanajärvi. The $\Delta^{14}\text{C}$ of the zooplankton in Lower Lough Erne supports this assertion. It is

consistent with that of the lake and river DOC, indicating that *E. gracilis* discriminates against sub-fossil carbon and detritus. $\Delta^{14}\text{C}$ values of *E. gracilis* in the summer when algae are more abundant show a clear switch to an algal diet, not indicated by the stable isotope results.

Daphnia, on the other hand, which have been proven to consume bulk POC (Pulido-Villena et al. 2005), are more depleted than the algal $\Delta^{14}\text{C}$. *Daphnia* have also been shown to feed on the algal portion of the POC (Rautio et al. 2011) but can also consume bacteria (Taipale et al. 2012). The ^{15}N values of *Daphnia* measured in this study are enriched relative to POC, but also to DOC, so the food source is unclear. However, their depleted $\Delta^{14}\text{C}$ values indicate that *Daphnia* in Lower Lough Erne are consuming a subfossil carbon source, suggesting that they may be feeding on bacteria, which are in turn consuming detrital subfossil carbon.

CONCLUSION

In this study, ^{14}C measurements have been used to determine the source of carbon utilized in the lake and the extent to which selected biota rely on terrestrial carbon support. The results of the study show that all carbon pools and hence the biota of Lower Lough Erne are supported by terrestrial carbon sources. The age of TC utilized in the food web has been determined in Lower Lough Erne, indicating that both detrital and labile TC are metabolized by invertebrates. However, sediment is predominantly derived from subfossil terrestrial carbon, indicating that exported subfossil TC may be stored in lake sediment while the majority of modern terrestrial carbon is mineralized in the food web, possibly leading to CO_2 saturation and flux to the atmosphere.

Lower Lough Erne is substantially supported by terrestrial carbon. Despite its heterotrophic status, carbon is still buried and stored in sediment. Further study is required to link production rates in Lower Lough Erne with carbon burial, but it is clear that seasonality in the terrestrial support of carbon pools in the lake is present and is best identified using $\Delta^{14}\text{C}$. The results from Lough Erne can be used to understand the propensity of an alkaline lake with terrestrial subsidy to be a source or store of terrestrial carbon, which in turn is linked with biotic processes in the lake. The ^{14}C method allows us to investigate the fate of catchment carbon exports in Lower Lough Erne, and globally in other lake types.

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